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to *Zonites cellarius*, *Zonites lucidus*, and *Zonites nitidulus*, it was not satisfactorily ascertained whether their heads were buried during the process of growth.

E. J. LOWE.

Observatory, Beeston,  
1854, February 14th.

- II. "Note on the Decomposition of Sulphuric Acid by Pentachloride of Phosphorus." By ALEXANDER WILLIAMSON, Ph.D., F.C.S., Professor of Practical Chemistry in University College. Communicated by Dr. SHARPEY, Sec. R.S. Received February 23, 1854.

Chemists have long been aware of the fact that some acids unite with bases in one proportion only, others in two or more proportions. Thus a given quantity of nitric acid forms with what is termed its equivalent of potash, a definite nitrate of potash; if less than this equivalent quantity of potash were added to the nitric acid, the product would be a mechanical mixture of the same nitrate of potash with uncombined nitric acid; if more than the equivalent of potash were added, the excess of alkali would remain uncombined. Sulphuric acid, on the other hand, is capable of forming two compounds with potash, and it depends upon the proportions in which the two substances are brought together whether the neutral or acid sulphate is formed.

The number of compounds which an acid forms with one base is now considered as indicating its atomic weight. The weights of sulphuric and nitric acids which are respectively susceptible of neutralizing the same quantity of potash are termed *equivalent*, but these are by no means the same as their *atomic* weights. Sixty-three parts of nitric acid (nitrate of water) contains the same quantity of hydrogen as forty-five parts of sulphuric acid, and when they are neutralized by potash the whole of this hydrogen is removed and replaced by potassium; and if neither of the acids could combine in any other proportion with potash, their atomic weights would be the same as their equivalent weights. But sulphuric acid also forms a potash compound in which half of its hydrogen is replaced by potas-

sium, the other half remaining in the compound, whereas the smallest particles of nitric acid either exchange the whole or none of their hydrogen for potassium.

This fact is expressed in the simplest possible manner by the statement that the smallest indivisible particles of sulphuric acid contain two atoms of hydrogen, whilst those of nitric acid only contain one. Thus it is, that whereas the equivalent weights of the two acids are the quantities which contain the same amount of basic hydrogen, their atomic weights must be in the proportion of two equivalents of sulphuric to one of nitric acid. The simplest expression for an atom of nitric acid being empirically  $\text{NO}_3 \text{H}$ , we shall accordingly represent an atom of sulphuric acid by the formula  $\text{SO}_4 \text{H}_2$ . In like manner, an atom of common phosphoric acid, being tribasic, is expressed empirically by the formula  $\text{PO}_4 \text{H}_3$ . The labours of Messrs. Laurent and Gerhardt greatly contributed to the establishment of these results, which are uncontroverted.

We have hitherto been accustomed to resort very freely to imaginary distinctions of form and arrangement of matter to explain the differences of properties; but of late years an opposite tendency has arisen, and chemists have felt the necessity of reducing their language and ideas to simpler and more consistent forms. This necessity was first felt in the most complex, *i. e.* the so-called organic part of chemistry. But the simplifications thus introduced have proved to be equally applicable to the inorganic part of the science; and their introduction is calculated to disengage, for the consideration of substantial differences of composition, the attention which has hitherto been absorbed by imaginary distinctions of form. Being unable to express the constitution of compounds without some formal artifice, we shall be able to see and compare their substantial differences most easily when all unnecessary variations of those formal artifices are eliminated. The success of this operation of course depends on our finding one form sufficiently general to replace the special and limited forms now employed.

In some papers published in the Journal of the Chemical Society two or three years ago, I endeavoured to show that the constitution of salts may be reduced to the type of water; that acids and bases being, truly, acid salts and basic salts, are perfectly conformable to the same principle; and that, amongst other things, the difference

between monobasic and bibasic acids, &c. admits of a simple and easy explanation by it. The leading propositions in those papers have been adopted by several eminent chemists in this country and in France; and M. Gerhardt speedily enriched science with a series of brilliant and striking illustrations of their truth. As regards the constitution of bibasic acids, M. Gerhardt's results were, however, at variance with that theory; and he was led to represent them by formulæ equally inconsistent with his own previous views on the subject. I believe that this discrepancy is satisfactorily removed by the facts I have the honour of submitting to the consideration of the Society.

An atom of nitric acid, being eminently monobasic, is, as we have already shown, represented in the monobasic type  $\begin{smallmatrix} \text{H} \\ \text{O} \end{smallmatrix}$  by the formula  $\begin{pmatrix} \text{NO}_2 \\ \text{H} \end{pmatrix} \text{O}$ , in which peroxide of nitrogen ( $\text{NO}_2$ ) replaces one atom of hydrogen. In like manner, hydrate of potash  $\begin{pmatrix} \text{H} \\ \text{K} \end{pmatrix} \text{O}$  is obtained by replacing one atom of hydrogen in the type by its equivalent of potassium; and nitrate of potash  $\begin{pmatrix} \text{NO}_2 \\ \text{K} \end{pmatrix} \text{O}$  by a simultaneous substitution of *one* atom of hydrogen by peroxide of nitrogen, the *other* by potassium. Sulphuric acid is formed from two atoms of

water  $\begin{smallmatrix} \text{H} & \text{O} \\ \text{H} & \\ \text{H} & \text{O} \\ \text{H} & \end{smallmatrix}$ ; one of hydrogen from each is removed, and the two replaced by the indivisible radical  $\text{SO}_2$ . The series

Sulphuric acid.      Acid sulphate of potash.      Neutral sulphate of potash.



explains itself.

Chemists have long known how to remove the basylous constituents H, K, &c. of these salts, and to replace them by others. But it is only recently that they have learnt to remove the chlorous radicals  $\text{SO}_2$ ,  $\text{NO}_2$ , &c. in a similar manner. To obtain the chloride of potassium from its sulphate, it is sufficient to bring the latter into liquid contact with chloride of barium; but the same reagent would be powerless for the preparation of the chlorides of the radicals  $\text{SO}_2$  or  $\text{NO}_2$ .

M. Cahours has shown us a reagent (the pentachloride of phosphorus) which is capable of forming from a great number of monobasic acids the chlorides of the acid radicals. Whilst extending our knowledge of the action of the body on monobasic and organic acids, and preparing numerous compounds of their radicals with one atom of chlorine, M. Gerhardt examined also the nature of its action upon bibasic acids and their compounds; and states that it consists of two successive phases, first, the liberation of the anhydrous acid, secondly, the substitution of two atoms of chlorine for one of oxygen in that anhydrous acid. These facts, if correct, would be unfavourable to the above view of the constitution of sulphuric and the other bibasic acids; and M. Gerhardt adopted accordingly the old formulæ, representing in their composition an atom of water ready-formed,  $\text{SO}_3\text{H}_2\text{O}$ .

Confining my remarks for the present to the case of sulphuric acid, whose decomposition is doubtless typical of that of other bibasic acids, I may state as the result of numerous experiments with the most varied proportions of pentachloride and acid, performed on a scale of considerable magnitude, that the first action of the pentachloride consists in removing one atom of hydrogen and one of oxygen (empirically peroxide of hydrogen) from the acid, putting in an atom of chlorine in their place and forming the compound  $\text{SO}_2 \overset{\text{H}}{\underset{\text{Cl}}{\text{O}}}$ , which is strictly intermediate between the hydrated acid and the final product  $\text{SO}_2\text{Cl}_2$  formed by a repetition of the same process of substitution of chlorine for peroxide of hydrogen. The existence and formation of this body, which we may call chloro-hydrated sulphuric acid, furnishes the most direct evidence of the truth of the notion, that the bibasic character of sulphuric acid is owing to the fact of one atom of its radical  $\text{SO}_3$  replacing or (to use the customary expression) being equivalent to two atoms of hydrogen. Had this radical been divisible like an equivalent quantity of a monobasic acid, we should have obtained a *mixture*, not a *compound* of the chloride with the hydrate,—or, at least, the products of decomposition of that mixture.

Chloro-hydrated sulphuric acid boils at  $145^\circ$  Cent., distilling without decomposition. The intensity of its action upon water varies according to the manner in which the two bodies are brought

together. When poured rapidly into a large quantity of cold water, a portion of it sinks to the bottom, and only gradually dissolves as a mixture of hydrochloric and sulphuric acids. When a small quantity of water is added to the compound, the same decomposition takes place with explosive violence. The acid dissolves chloride of sodium on the application of a gentle heat with evolution of hydro-

chloric acid, giving rise to a compound of the formula  $\text{SO}_2 \overset{\text{Na}}{\underset{\text{Cl}}{\text{O}}}$ . When

poured upon pieces of melted nitre at the atmospheric temperature, an effervescence takes place with evolution of a colourless vapour which possesses in a striking degree the odour of aqua regia. This vapour may be dissolved in various liquids, and when decomposed by water, yields nitric and hydrochloric acids. It is doubtless chloro-nitric acid,  $\text{NO}_2 \text{Cl}$ . In like manner the chlorides of other inorganic acid radicals may be obtained, as from chlorates, perchlorates, sulphites, &c., but of these and other reactions I beg leave to defer any further account until the experiments now in hand are more advanced.

From the general resemblance of properties and identity of boiling-point of the chloro-hydrate with a compound discovered by Rose, and described by that eminent chemist as possessing empirically the composition  $\text{S}_2 \text{O}_5 \text{Cl}_2$ , I was led to suspect that the two might in reality be identical, which of course would require the addition of the elements of water to Rose's formula, and several experiments I have performed afford strong confirmation of that identity. The same compound is obtained by the action of dry hydrochloric acid on anhydrous sulphuric acid; and finally, I may mention that Mr. Railton obtained a small quantity of the same substance some weeks ago in my laboratory by the action of platinum-black at a high temperature on an imperfectly dried mixture of chlorine and sulphurous acid.

As regards the successive transformations effected in the pentachloride, I have observed the formation of Wurtz's oxychloride (the tribasic chloro-phosphoric acid ( $\text{PO Cl}_3$ )), and also of a compound boiling above  $145^\circ$ , probably  $\text{PO}_2 \text{Cl}$ . Hydrated phosphoric acid is always found unless the amount of pentachloride added is very great.